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Application of Methods 606 and 608 for
Analysis of PCBs, Organochlorine Pesticides and
Phthalate Esters Contained in Landfill Leachates

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APPLICATION OF METHODS 606 & 608
FOR ANALYSIS OF PCBs, ORGANOCHLORINE PESTICIDES
AND PHTHALATE ESTERS CONTAINED IN LANDFILL LEACHATES

by

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and

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OFFICE OF RESEARCH AND DEVELOPMENT
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CINCINNATI, OHIO 45268

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report describes the application of EPA Methods 606, Phthalate Esters, and 608, Chlorinated Pesticides and PCBs to the analysis of a sanitary landfill leachate. This report will be useful for identifying problem areas in the determination of phthalate esters, pesticides and PCBs in leachate matrices.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

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ABSTRACT

Leachates collected from a sanitary landfill were spiked with a variety of phthalate esters, polychlorinated biphenyls and organochlorine pesticides. The spiked leachates were then analyzed according to priority pollutant methods 606 and 608. Accuracy, precision and method detection limits were calculated from the resulting analyses. It was determined that method 608 worked well for organochlorine pesticides. The method detection limit varied between 0.02 and 0.3 $\mu\text{g/L}$ for the pesticides tested with accuracy and precision data similar to those obtained from spiked reagent water. Poor recoveries were obtained for phthalate esters and polychlorinated biphenyls. Method detection limits for phthalate esters ranged between 10 and 30 $\mu\text{g/L}$ and for polychlorinated biphenyls (Aroclor 1260) 1 $\mu\text{g/L}$. This report covers the time period from December 1980 through May 1981. The work was completed as of June 1981.

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SECTION 1

INTRODUCTION

Methods 606 and 608 are liquid/liquid extraction electron capture gas chromatography methods currently used by the Agency for the determination of polychlorinated biphenyls, organochlorine pesticides and phthalate esters contained in industrial and municipal wastewaters. The purpose of this ongoing study is to determine if these and other procedures are applicable to the determination of priority pollutants in landfill leachates.

Leachate samples were collected from a large sanitary landfill located in Hamilton County, Ohio. The site is an active landfill using the "Area" method of landfilling. The leachate runs out from the landfill through a pipe that extends approximately 10 meters into an 11-year-old fill area. Samples are collected directly from the discharge of the pipe. The leachate collected represents all sources of water that have percolated through the landfill. For this study, samples were collected in 4-liter amber glass bottles, sealed with Teflon lined screw caps, and stored at 4°C until the time of analysis. In contrast to other leachates supplied to this laboratory by Regional laboratories, this was a rank complex mixture that contained suspended solids, had a pH 7-6, was light brown in color and foamed.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The landfill leachate studied contained a complex mixture of extractable chemical compounds. Analysis of such extracts without cleanup will irreversibly damage the GC column. For Method 606, recoveries in excess of 70% should be expected with poor relative standard deviation (RSD) for duplicate analyses. Method detection limits for the various phthalate esters range between 10 and 30 $\mu\text{g/liter}$. At concentrations in excess of 0.5 $\mu\text{g/L}$, Method 608 worked well for the pesticides tested. The recoveries and RSD for duplicate analyses were comparable to reagent water spikes. The method detection limit (MDL) for the organochlorine pesticides tested, ranged between 0.02 and 0.3 $\mu\text{g/liter}$.

Poor recoveries, 30 to 40% less than those for reagent water spikes, were noted for the PCBs. The reason for the poor recovery is as yet unknown. The MDL for Aroclor 1260 is below 1 $\mu\text{g/liter}$.

Landfill leachates should be collected from other sources and this study repeated to determine if a representative leachate was selected for this study. Sample preservation techniques should be investigated to determine if the poor PCB recoveries are due to degradation of the spiked samples. Additional studies for remaining methods and parameters should be initiated as personnel are available.

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SECTION 3

EXPERIMENTAL

One-liter samples were extracted exactly according to Methods 606 and 608. The extracts were then subjected to Florisil column cleanup to minimize interference problems. All extracts were analyzed by injecting one to three μ L of the extracts into a gas chromatograph equipped with an electron capture detector.

The analytical column was a 1.8 M long by 4 mm ID glass column packed with 1.5% SP 2250/1.95% SP 2104 on 100/120 mesh Supelcoport. The column was operated isothermally at 185 $^{\circ}$ with an argon + 5% methane carrier gas at a flow rate of 60 mL/minute. The on-column injector was maintained at 195 $^{\circ}$ C and the linearized electron capture detector at 230 $^{\circ}$ C. Quantitation was based upon the chromatographic peak height comparison of the standard responses to the sample extract responses.

Leachates were spiked with various priority pollutants at approximately 10 times the method detection limit (MDL) of reagent water. If background interferences for individual compounds were noted at these levels, the leachates were then spiked at higher levels within the dynamic range of the detector.

Twenty-four hours before extraction, the leachate was mixed in a large container, then aliquots were placed into 1-L bottles. One mL of an acetone spiking solution containing mixtures of the priority pollutants was added to each aliquot. The bottles were then sealed, shaken for one minute, then stored at 4 $^{\circ}$ C for 18 to 24 hours. The spiked samples were allowed to warm to room temperature before extraction.

QUALITY CONTROL

Whenever possible, spiking solutions were prepared from pesticides and PCBs obtained from the U.S. EPA pesticide repository. With each series of extractions, a reagent blank and a spiked reagent water was analyzed to monitor the quality of reagents and to insure that the laboratory was obtaining acceptable recoveries as specified within the Method being investigated. Quality Assurance Branch quality control samples were analyzed to validate standard solutions. Standards were prepared from spiking solutions by diluting 1.0 mL of the spiking solution to 10.0 mL with hexane. Statistically significant numbers of samples were spiked and extracted in order to determine recoveries. Methods 606 and 608 were followed according to the

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procedure by a qualified analyst.

RESULTS

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Analysis of the nonspiked leachate by Methods 606 and 608 produced complex electron capture chromatograms throughout the elution area of the priority pollutants. GC/MS analysis identified the presence of a number of diverse organic compounds. Of the target priority pollutants, only dibutylphthalate, di-2-ethylhexylphthalate, and dioctylphthalate were identified.

After analyzing the raw extracts, it was found through the quality control program that endrin and p,p'-DDT would no longer elute from the column. Endrin and p,p'-DDT eluted from standard injections after conditioning the column for several days. However, when comparisons were made to prior analyses, area responses were depressed and the peak geometry for both compounds was unacceptable. Thus, the raw leachate extracts were submitted to Florisil cleanup as outlined in Methods 606 and 608, the analytical GC column repacked, and the extracts reanalyzed. The resulting chromatograms were greatly improved and the column performance for endrin and p,p'-DDT was not adversely affected. Table 1 shows the accuracy and precision for the phthalate esters (Method 606). Dimethyl phthalate could not be analyzed in the leachate extracts because of nonresolvable interferences.

The average recoveries for dibutyl phthalate, butylbenzyl and di-2-ethylhexyl phthalate from this complex sample matrix appears to be within an acceptable accuracy range of 81 to 95%. However, the relative standard deviation (RSD) of 43 to 67% for these compounds indicates that the precision of the method for these analytes in this leachate is unacceptable and above the MDL. The MDL data appearing in this table were calculated from these spiked recoveries. No high level spiked precision and accuracy study was obtained.

Table 2 lists the accuracy and precision for the organochlorine pesticides spiked into the leachate at two different levels. The lower levels (0.5 to 1.5 µg/L) were spiked at approximately 10 times the MDL for reagent water and about five times the background values. The results from these low level spikes show that these values are near the MDL for pesticides in this landfill leachate. Therefore, the MDL data appearing in this table were calculated from these low level spikes. The laboratory reagent water control data indicated that the higher MDL is due to the high leachate background and not to the laboratory operations. At higher spiking levels, 0.5 to 1.5 µg/L, the recoveries were comparable to the lab control. The RSD varied between 3 and 9% which is acceptable for such a complex matrix.

For the PCBs, an accuracy and precision study was conducted using a spiking solution containing Aroclors 1242 and 1260. This mixture contained a multitude of chlorinated biphenyl isomers from C₁₁ through C₁₈. The samples were spiked at 1.48 µg/L Aroclor 1242 and 1.18 µg/L Aroclor 1260. The GC elution area of the PCB spiked leachate for Aroclor 1242 (C₁₁ through C₁₄ PCB isomers) proved to be too complex for meaningful data reduction even after the extracts were submitted to clean up techniques as

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described in Method 608. The elution area for the PCBs contained in Aroclor 1260 (C15 through C18 isomers) was relatively interference free. Table 3 lists the spike concentrations and the accuracy and precision obtained from the PCB spiked leachate. The recoveries for individual PCB isomers were determined (peaks A through P) as well as the recovery for the Aroclor 1260. It is apparent from these data that the recoveries for the individual PCB from spiked leachates are 30 to 40% low when compared to reagent water. The relative standard deviations are high but acceptable for such a complex matrix. Based upon literature reports and past experiences, the high suspended solids content of the leachate was believed to cause low PCB recoveries. In an effort to establish this, reagent water containing 0, 0.25 and 0.5 g/L of humic acid was spiked with the PCB mixture. Table 4 shows the resulting recoveries. It is apparent from this study that the poor PCB recoveries for spiked leachates are not likely due to the humic acid content of the leachate. Sufficient time was not available to determine recoveries upon spiked filtered leachates or spiked preserved leachates to properly identify the reason for the poor PCB recoveries.

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Table 1. ACCURACY AND PRECISION FOR PHTHALATE ESTERS
SPIKED INTO LANDFILL LEACHATE

Phthalate Ester	Spike Level µg/L	MDL ^a µg/L	Spiked ^b Leachate		Laboratory Control Spiked Reagent Water	
			Recovery %	R.S.D. %	Recovery %	R.S.D. %
Dimethyl	12.9	--	Interference		112	14
Diethyl	11.4	20.5	130	38	106	11
Di n-Butyl	12.2	26	96	57	119	14
Butylbenzyl	6.4	8.3	81	43	119	10
Diethylhexyl	11.6	24.4	85	67	125	12

^a Method Detection limit for spiked leachate based upon the Standard Deviation obtained from these data.

^b Average of 6 values less blanks.

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Table 2. ACCURACY AND PRECISION FOR ORGANOCHLORINE PESTICIDES
SPIKED INTO LANDFILL LEACHATE

Pesticide	Spike Level µg/L	Spiked Leachate		Lab Control	
		% Recovered	RSD	% Recovered	RSD
γ-BHC	0.51	95	4	85	1
Heptachlor	0.50	73	9	63	0.3
Aldrin	0.49	79	5	73	0.3
Endosulfan-1	1.48	84	3	87	0.7
Dieldrin	0.99	85	3	87	0.5
Endrin	1.00	87	5	79	0.2
Endosulfan-2	1.49	59	7	59	23

Pesticide	Spike Level µg/L	Spiked Leachate		MDL ^a µg/L	Lab Control	
		% Recovered	RSD		% Recovered	RSD
α-BHC	.036	63	39	.03	114	5
Heptachlor	.037	89	25	.03	99	4
Aldrin	.030	109	16	.02	103	4
Endosulfan-1	.081	187	48	.2	103	6
Dieldrin	.056	93	13	.03	105	6
Endrin	.058	88	10	.02	98	5
Endosulfan-2	.082	84	37	.1	115	7

^a MDL calculated from spiked leachate

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Table 3. ACCURACY AND PRECISION FOR PCBS SPIKED
INTO LANDFILL LEACHATE

Compound PCB	Spike Level µg/L	Spiked Leachate		Spiked Reagent Water	
		% Recovery	R.S.D.	% Recovery	R.S.D.
A	Aroclor 1242 1.48	a		74	12
B		a		86	13
C		a		91	5
D		a		82	4
E		a		99	3
F		a		105	1
G		a		92	4
H		a		99	5
I	Aroclor 1260 1.15	73	10	103	1
J		68	10	92	3
K		58	17	91	4
L		62	12	101	4
M		61	11	97	5
N		63	9	104	4
O		58	11	98	2
P		54	14	99	1
Combined peaks as 1260		62	10	98	5

^aToo much leachate blank interference for accurate measurement of spike samples.

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Table 4. ACCURACY AND PRECISION FOR PCBS SPIKED
INTO HUMIC ACID SOLUTIONS

Compound	Spike Level µg/L	0.25 g/L Humic Acid		0.50 g/L Humic Acid		Spiked Distilled Water	
		Avg. R.S.D.		Avg. R.S.D.		Avg. R.S.D.	
Aroclor 1242	1.48						
Peak A		104	7	109	4	90	14
B	0-1/2"	103	7	103	7	97	2
C		104	7	103	6	98	6
D		108	8	116	3	102	4
E	9-1/8"	102	10	112	2	97	2
F		103	14	114	2	99	1
G		103	6	109	6	98	3
H		104	11	111	3	103	5
Aroclor 1260	1.15						
Peak I		100	7	94	5	101	1
J		98	7	94	4	98	1
K		95	6	96	10	94	3
L		100	8	104	9	96	4
M		85	11	93	8	96	5
N		91	9	97	2	95	6
O		90	3	100	4	80	2
P		91	9	93	4	87	1

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